

ELECTROLYTIC CAPACITOR

TECHNICAL FIELD

The present invention relates to an electrolytic capacitor, the electrolyte of the capacitor is an ionic
5 conductive solid electrolyte including polymer.

BACKGROUND ART

FIG. 3 shows a partially sectional perspective view of
10 a conventional electrolytic capacitor. Capacitor element 29
is formed by positive foil 21 and negative foil 22, wound
together with intervening separator 23. Positive foil 21 is
an aluminum foil, the effective surface area of foil 21 has
been enlarged through etching process, and a dielectric oxide
15 film formed through a chemical process is provided on the
surface. Negative foil 22 is also made of an etched aluminum
foil. Positive foil 21 and negative foil 22 are connected,
respectively, with positive lead 25 and negative lead 26.
Capacitor element 29 is impregnated with electrolyte 24 for
20 driving. Capacitor element 29 is inserted in metal case 28
of aluminum, etc., and case 28 is sealed with sealing plate
27 made of rubber or the like material to complete a finished
electrolytic capacitor.

An ionic conductive liquid is used for electrolyte 24;
25 for example, an organic solvent of ethylene glycol, γ -
butyrolactone, etc., in which boric acid, ammonium borate, etc.
is resolved as solute. The content of water in electrolyte
24 is reduced, when solute of azelaic acid, 1,6-decane

dicarboxylic acid, 5,6-decane dicarboxylic acid, dioic acids having a side chain or nonaqueous salts of the acids are used. Using such solute, the unclosing of electrolytic capacitors due to an increased inner pressure caused by the water content in the environment hotter than 100°C can be curtailed.

There are other electrolytic capacitors which use an electronic conductive solid electrolyte in place of liquid electrolyte 24. Polypyrrole, polythiophene, polyaniline, etc. are used as the electrolyte. These electrolytes offer the advantages of lower equivalent serial resistance (hereinafter referred to as ESR). Thus it implements an electrolytic capacitor having a low ESR and a superior impedance characteristic.

There is still other proposal of using an ionic conductive solid electrolyte; the electrolyte is divided into the inorganic and the polymeric. The inorganic electrolyte has the advantage of high ionic conductivity; however, it is heavy, inflexible and less plastic. On the other hand, the polymeric electrolyte is attracting the attentions because it is light in weight and has superior mechanical properties such as flexibility, plasticity, etc.; despite its disadvantage in the lower ionic conductivity as compared to the inorganic electrolyte.

In the electrolytic capacitors using the ionic conductive polymer electrolyte, gelled electrolyte layer is formed between a positive foil having dielectric oxide film and a negative foil. Japanese Patent Unexamined Publication No. H09-082580 discloses an electrolytic capacitor using the

gelled electrolyte of the following ingredients:

(a) a thermoplastic elastomer selected from among the polyamide-polyether block polymer and polyester-polyether block polymer,

5 (b) a polar organic solvent, and

(c) a solute.

According to Japanese Patent Unexamined Publication No. H10-223481, a positive foil and a negative foil provided at the surface with pits having the diameters larger than 0.1 μ m are wound together with an intervening separator containing polyvinyl alcohol, for forming a capacitor element. The capacitor element is put into contact with a liquid electrolyte containing ethylene glycol for electrolytic capacitor, and the liquid electrolyte is gelled.

15 Electrolytic capacitors for use in nowadays countermeasure circuits against higher harmonics and in vehicles are requested to have a higher withstanding voltage, a higher heat resisting property, a longer life and a higher reliability in the anti-vibration capability, as compared to conventional electrolytic capacitors. The conventional liquid electrolytes using ionic conductive liquid can not satisfy the requirements in terms of the higher withstanding voltage ratio (improved spark voltage), the higher heat resisting temperature and the longer life.

25 The ionic conductive polymeric electrolyte has a high withstanding voltage, but the ionic conductivity is low as compared with the liquid electrolyte. As the result, resistance of electrolyte itself is high, which leads to a

greater resistance loss as a capacitor. Therefore, it is important to reduce the resistance of the separator. Manila papers, kraft papers, esparto papers, etc., which are the materials generally used for the separator in aluminum electrolytic capacitors, have a high density. If, a lower density version of these materials is used for the purpose of lowering the resistance, the anti-short circuiting capability and the tensile strength are not enough.

10 SUMMARY OF THE INVENTION

An electrolytic capacitor in the present invention includes a positive foil provided at the surface with a dielectric film, a negative foil, and a separator therebetween containing polymeric electrolyte composite. The polymeric electrolyte composite contains an electrolyte in the matrix of acrylic ester copolymer. The electrolyte is consisting of a polar solvent, and a solute containing neither metal ion nor quaternary ammonium ion as a cation. The acrylic ester copolymer is a polymer of first monomer and second monomer. The first monomer is an acrylic derivative of at least one among the group of monofunctional monomers having hydroxyl group at the end and one polymeric unsaturated double bond. The second monomer is an acrylic derivative of at least one among the group of multifunctional monomers having a plurality of polymeric unsaturated double bonds. The separator includes at least either one among the rayon fiber and the cotton linter. Or, the separator is formed of a plurality of cellulose fiber sheets overlaid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the front elevation, partially cut-off, of an electrolytic capacitor in accordance with an exemplary embodiment of the present invention.

FIG. 2 is a partially-sectional perspective view showing the structure of the electrolytic capacitor shown in FIG. 1.

FIG. 3 is a partially-sectional perspective view of a conventional electrolytic capacitor.

DESCRIPTION OF PREFERRED EMBODIMENT

FIG. 1 is a partially cut-off front elevation of an electrolytic capacitor in accordance with an exemplary embodiment of the present invention, used to show the structure.

FIG. 2 shows the perspective view, partially cut-off. Capacitor element 11 is formed by positive foil 11A and negative foil 11C opposing to each other, which are wound together with intervening separator 11S. Positive foil 11A is an aluminum foil, the effective surface area of foil 11A is enlarged through etching process and the surface is provided with a dielectric oxide film formed through anode oxidation process. It is provided with positive lead 12. Negative foil 11C is also formed of an etched aluminum foil, and provided with negative lead 13.

Capacitor element 11 is impregnated with a liquid which forms an ionic conductive polymeric electrolyte composite (hereinafter referred to as electrolyte composite) 14. The element is inserted in metal case 16 made of aluminum, and the

opening of the metal case is closed with sealing plate 15.

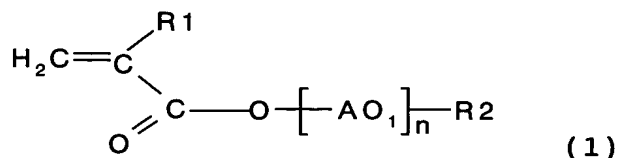
When metal case 16 is heated, electrolyte composite 14 is formed within the inside and the outer surface of capacitor element 11, and on the inner surface of metal case 16.

5 Capacitor element 11 is thus fixed in the inside of metal case 16 to form a finished electrolytic capacitor. Metal case 16 is covered with covering resin 17.

The liquid for forming electrolyte composite 14 contains two kinds of acrylic ester monomers and a polymerization
10 initiator. The acrylic ester monomers cause radical polymerization as the result of heating. Thereby, a matrix of copolymer is formed. The liquid for forming electrolyte composite 14 contains either one or more of inorganic acids, organic acids or salts of the one of the acids as the solute,
15 and the polar solvent. Therefore, the solute and the polar solvent are taken into the crosslinked matrix of copolymer. Electrolyte composite 14 has such a structure. The polymerization initiator is such organic peroxide as, for example, t-butylperoxyacetate, t-butylperoxybenzoate, t-
20 hexylperoxy-2-ethylhexanate, t-hexylperoxybutylate, t-butyl peroxy maleate.

Materials for forming such electrolyte composite 14 are practically described below. A first acrylic ester monomer (first monomer) is an acrylic derivative of at least one among
25 the group of monofunctional monomers having hydroxyl group at the end and one polymeric unsaturated double bond. The first monomer shows a better affinity with solvent than acrylic ester having alkyl group at the end. As a result, the matrix of

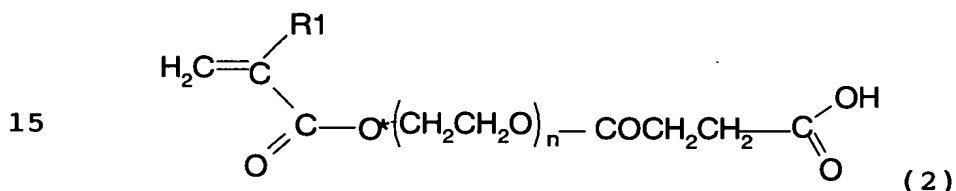
crosslinked copolymer readily takes in the polar solvent, in which either one or more of inorganic acids, organic acids or salts of the one of the acids is resolved. This leads to a higher ionic conductivity. The following can be used for the first monomer.



R1 : H or alkyl group having the number of carbons 1 - 5

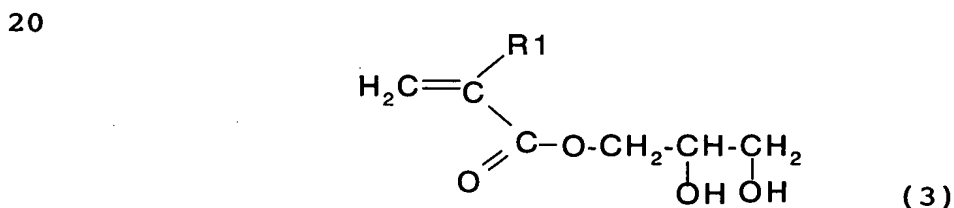
10 AO₁ : Alkylene oxide group having the number of carbons 2 - 4

n : Average additional mole number (1 - 200) of alkylene oxide group having the number of carbons 2 - 4

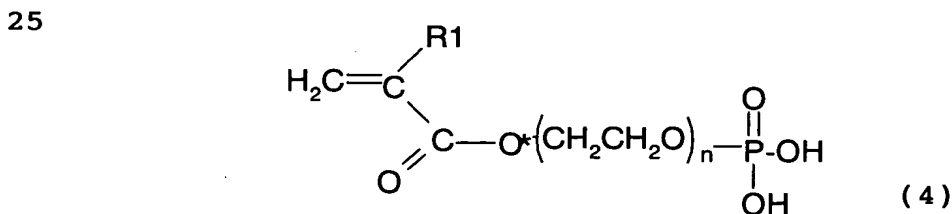


R1 : H or alkyl group having the number of carbons 1 - 5

n : Average additional mole number (1 - 200) of alkylene oxide group having the number of carbons 2

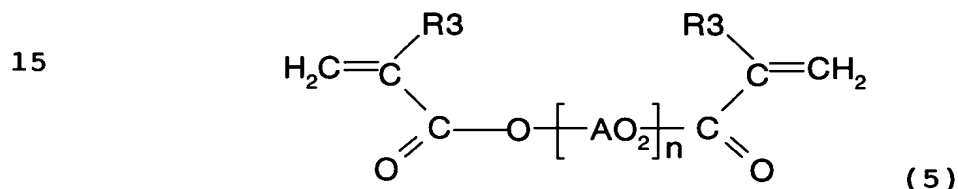


R1 : H or alkyl group having the number of carbons 1 - 5



R1 : H or alkyl group having the number of carbons 1 - 5

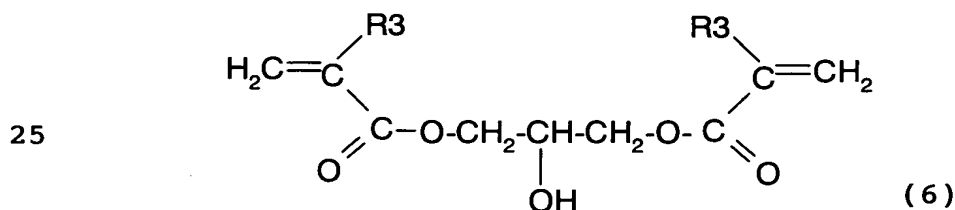
A second acrylic ester monomer (second monomer) is an acrylic derivative of at least one among the group of multifunctional monomers having a plurality of polymeric
5 unsaturated double bonds. The second monomer improves the affinity of the matrix of copolymer with the solvent, and the crosslinking density. This increases the quantity for containing the liquid electrolyte. Thus, the ionic conductivity is further increased. Since the matrix of
10 copolymer maintains a certain physical distance between the electrodes, the electrolytic capacitors exhibit a superior anti-short circuiting property. The following can be used for the second monomer.



R3 : H or alkyl group having the number of carbons 1 - 5

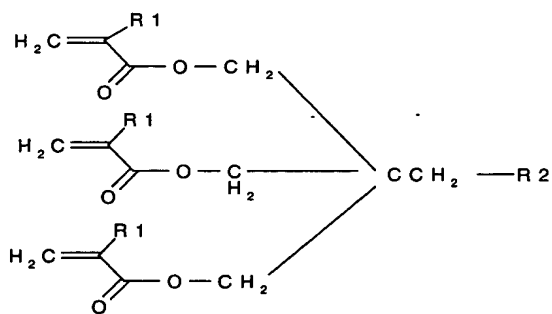
AO₂ : Alkylene oxide group having the number of carbons 2 - 4

20 n : Average additional mole number (1 - 200) of alkylene oxide group having the number of carbons 2 - 4



R3 : H or alkyl group having the number of carbons 1 - 5

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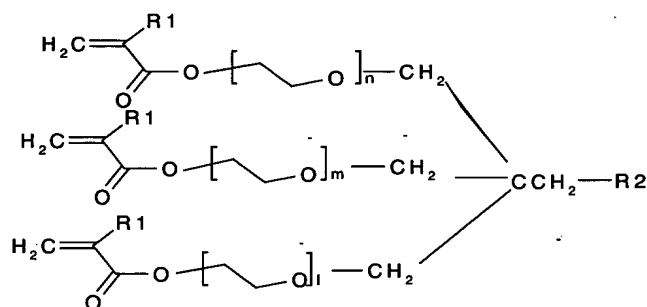
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R1 : H or alkyl group having the number of carbons 1 - 5

R2 : H or alkyl group having the number of carbons 1 - 5

R1 and R2 may either be the same or different to each other.

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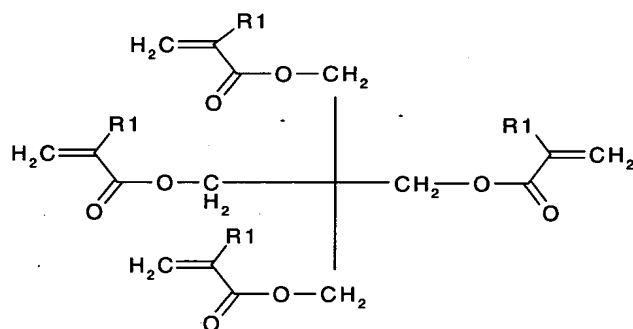
(8)

R1, R2 : H or alkyl group having the number of carbons 1 - 5

R1 and R2 may either be the same or different to each other.

l, m, n : Average additional mole number (1 - 200) of alkylene oxide group having the number of carbons 2

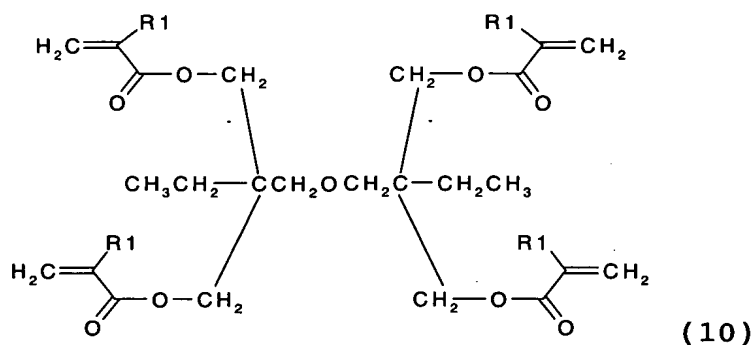
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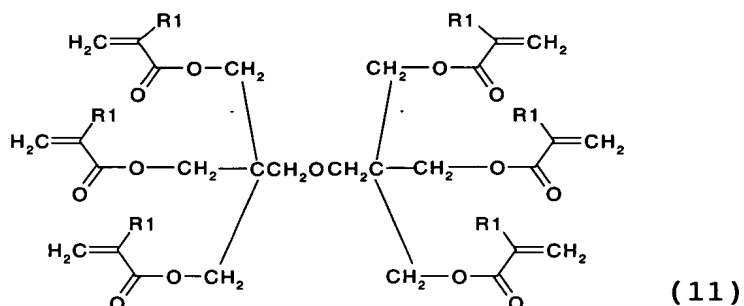
R1 : H or alkyl group having the number of carbons 1 - 5

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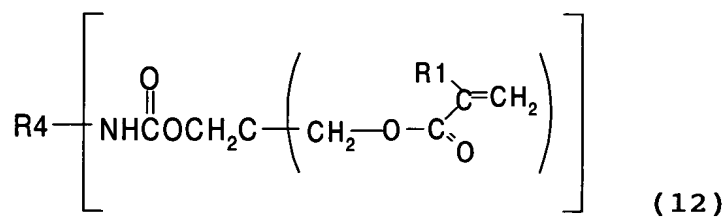
R1 : H or alkyl group having the number of carbons 1 - 5

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15 R1 : H or alkyl group having the number of carbons 1 - 5

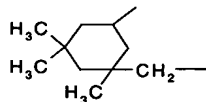
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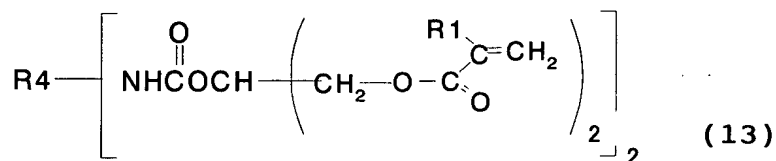
R1 : H or alkyl group having the number of carbons 1 - 5

R4 : - (CH₂)_n - , - (C₂H₄O)_n -

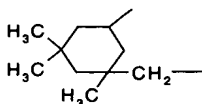
n is a natural number 1 - 9.



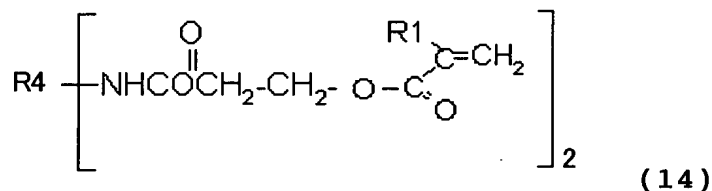
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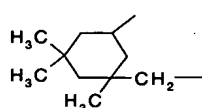
R1 : H or alkyl group having the number of carbons 1 - 5

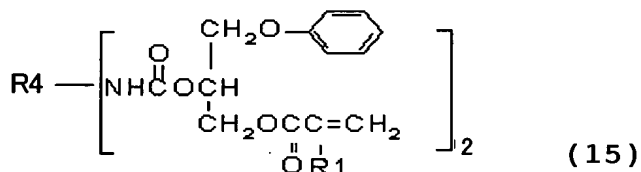
R4 : - (CH₂)_n - , - (C₂H₂O)_n - , 
 n is a natural number 1 - 9.

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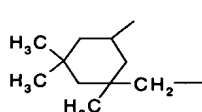


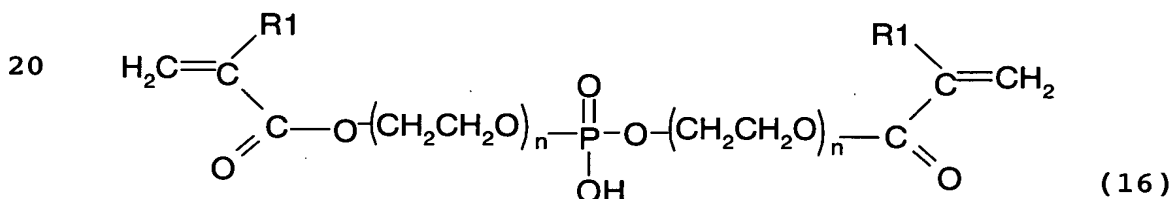
R1 : H or alkyl group having the number of carbons 1 - 5

10 R4 : - (CH₂)_n - , - (C₂H₂O)_n - , 
 n is a natural number 1 - 9.



15 R1 : H or alkyl group having the number of carbons 1 - 5

R4 : - (CH₂)_n - , - (C₂H₂O)_n - , 
 n is a natural number 1 - 9.



R1 : H or alkyl group having the number of carbons 1 - 5
 n is a natural number 1 - 9.

25 The carbons 6 or more numbers with R1, R2 or R3 deteriorates the affinity with solvent. The carbons 5 or more numbers with AO₁ deteriorates the affinity with solvent. The average additional mole number 200 or more with l,m or n

causes a higher viscosity, which leads to a difficulty of impregnation. The n number 10 or more with R4 causes a higher viscosity, which leads to a difficulty of impregnation.

The following may be used for the polar solvent :

5 Ethylene glycol, propylene glycol, 1,4-butanediol, glycerin, polyoxyalkilenepolyol (polyethylene oxide, polypropylene oxide or polyoxyethylene-oxypropylene glycol of which molecular weight is at most 200 and mixture thereof), amide solvent such as N-methylformamide, N,N-dimethylformamide, 10 N-methylacetamide or, N-methylpyrrolidinone, alcohol solvent such as methanol or ethanol, ether solvent such as methylal, 1,2-dimethoxyethane, 1-ethoxy-2-methoxyethane or 1,2-diethoxyethane, nitrile solvent such as acetonitrile or 3-methoxypropionitrile, furan solvent such as 2,5- 15 dimethoxytetrahydrofuran, sulfolane solvent such as sulfolane, 3-methylsulfolane or 2,4-dimethylsulfolane, carbonate solvent such as propylene carbonate, ethylene carbonate, diethyl carbonate, styrene carbonate, dimethyl carbonate or methylethyl carbonate, lactone solvent such as γ -butyrolactone, 20 γ -valerolactone, δ -valerolactone, 3-methyl-1,3-oxazolidine-2-one or 3-ethyl-1,3-oxazolidine-2-one, imidazolidinone solvent such as 1,3-dimethyl-2-imidazolidinone, or pyrrolidone solvent.

Each of these may be used by itself alone, or in combination 25 of two or more. Preferred among these are ethylene glycol, propylene glycol, diethylene glycol, water, lactone solvent, alcohol solvent, carbonate solvent, ether solvent, nitrile solvent and furan solvent.

As for the inorganic acid or organic acid, the following may be used :

polycarboxylic acid (bivalent, tervalent or quadrivalent):

aliphatic polycarboxylic acid (saturated polycarboxylic acid) such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,6-decanedicarboxylic acid, 5,6-decanedicarboxylic acid, 1,7-octanedicarboxylic acid, 7-methyl-7-methoxycarbonyl-1, 9-decanedicarboxylic acid, 7,9-dimethyl-7,9-dimethoxycarbonyl-1,11-dodecanedicarboxylic acid, or 7,8-dimethyl-7,8-dimethoxycarbonyl-1,14-tetradecanedicarboxylic acid

unsaturated polycarboxylic acid such as maleic acid, fumaric acid or itaconic acid

aromatic polycarboxylic acid such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, or pyromellitic acid

alicyclic polycarboxylic acid such as tetrahydrophthalic acid (cyclohexane-1, 2-dicarboxylic acid or the like) or hexahydrophthalic acid

alkyl (the number of carbons is 1 to 3) or nitro substitution product of these polycarboxylic acid such as citraconic acid, dimethylmaleic acid, nitrophthalic acid (3-nitrophthalic acid, 4-nitrophthalic acid)

polycarboxylic acid containing sulphur such as thiopropionic acid

mono carboxylic acid:

aliphatic monocarboxylic acid (saturated
monocarboxylic acid, the number of carbons is 1 to 30 thereof)

such as formic acid, acetic acid, propionic acid, butyric acid,
isobutyric acid, valeric acid, caproic acid, enanthic acid,
5 caprylic acid, pelargonic acid, lauric acid, myristic acid,
stearic acid, behenic acid, malic acid, or tartaric acid

unsaturated monocarboxylic acid such as acrylic acid,
methacrylic acid or oleic acid

aromatic monocarboxylic acid such as benzoic acid,
10 o-nitrobenzoic acid, p-nitrobenzoic acid, cinnamic acid or
naphthoic acid

oxycarboxylic acid such as salicylic acid, mandelic acid
or resorcylic acid

boric acid, phosphoric acid, silicotungstic acid,
15 silicomolybdic acid, phosphomolybdic acid.

These and the salts of these can be used as the solute. Among
others, 4-fluoboric acid, 6-fluophosphoric acid, perchloric
acid, trifluoromethane sulfonic acid and their salts are for
electrical double layer capacitors.

20 In view of the anti-short circuiting property at high
voltage, no metal ion is contained in the solute. From the
view point of chemical stability, no quaternary ammonium ion
is contained in the solute. When quaternary ammonium salt is
used, the deterioration induces liquid leakage; thus there is
25 a problem in the safety.

There are salts including carbocation or oniniumcation
such as sulfonium cation or phosphonium cation. In practice,
the solute should preferably be at least one of salts of

inorganic and organic acids selected from the group of ammonium salt, primary amine salt, secondary amine salt, tertiary amine salt or amidine salt. These are superior in ionic conductivity, and maintain the stable characteristics even after they are
5 deteriorated.

The amine constituting amine salt includes
primary amine such as methylamine, ethylamine, propylamine, butylamine, ethylenediamine,
secondary amine such as dimethylamine, diethylamine,
10 dipropylamine, methyl-ethylamine, diphenylamine, diethanolamine,

tertiary amine such as trimethylamine, triethylamine, tripropylamine, tridiphenylamine, triethanolamine. As the amidine salt, compound including alkyl-substituted amidine,
15 imidazole compound, benzoimidazole compound or alicyclic amidine compound based on quaternary compound including alkyl-substituted amidine made quaternary by alkyl group or arylalkyl group including 1 to 11 carbons are named.

Describing more practically; quaternary compound
20 including alkyl-substituted amidine:

1-methyl-1,8-diazabicyclo[5,4,0]undec-7-ene-1-methyl-1,5-diazabicyclo[4,3,0]non-5ene-1,2,3-trimethylimidazolium, 1,2,3,4-tetramethyl-imidazolium, 1,2-dimethyl-3-ethyl-imidazolium, 1,3-dimethyl-2-heptyl-imidazolium, 1,3-dimethyl-2-(-3'-heptyl)imidazolium, 1,3-dimethyl-2-dodecyl-imidazolium, 1,2,3-trimethyl-1,4,5,6-tetrahydro-pyrimidium, 1,3-dimethyl-imidazolium, 1-methyl-3-ethyl-imidazolium, 1,3-dimethylbenzo imidazolium are

named.

Now, separator 11S is described. A rayon fiber or a cotton linter is used for separator 11S. The rayon fiber is a round fiber of several μ m having fibril net structure. The cotton linter is a short fiber, although it is rather thicker than rayon fiber. Because of such properties, these fibers provide greater surface area than other fibers when skimmed to form a separator sheet; which means that they can contain the electrolyte for more quantities. The ion transmission in electrolyte composite 14 is blocked less, so the resistance loss of the capacitor is small. Since rayon fibers are structured of micro fibers having numerous adhesion points, they are advantageous in terms of anti-short circuiting performance. Electrolytic capacitors using these separators implement a high withstanding voltage, a high thermal resistance, a longer life and a higher operational safety.

Separator 11S may be formed instead with a sheet of rayon fiber or cotton linter containing at least one of cellulose fibers. Or, these may be overlaid to form a separator. The separator made of mixture of those fibers or of overlaid sheets provides a higher fiber-to-fiber density than a sheet of rayon fiber, or cotton linter, alone. This provides a further advantage for the ion transmission in electrolyte composite 14. As to the cellulose fibers, at least one among Manila jute, kraft, hemp and esparto may be used. These can be used in common also for electrolytic capacitors which use liquid electrolyte. So, it offers cost merits.

Still further, separator 11S may be formed instead by

overlaying a sheet of rayon fiber, or cotton linter, and a sheet of a cellulose fiber, or the mixture. A separator of the overlaid sheets doesn't block the ion transmission in electrolyte composite 14, and offers an improved anti-short
5 circuiting performance.

Still further, separator 11S may be formed instead by overlaying a sheet of rayon fiber, or cotton linter, containing at least one among Manila jute, kraft, hemp and esparto, and a sheet of at least one of cellulose fibers. A separator of
10 the combination sheets doesn't block the ion transmission in electrolyte composite 14, and offers an improved anti-short circuiting performance.

Still further, separator 11S may be formed instead by overlaying sheets made of one or more kinds of cellulose fibers.
15 A separator formed by overlaying two, or three, low density cellulose sheets exhibits an intense fiber-to-fiber gap that is apparently finer than that of a single sheet of the same basis weight. Since the arrangement of overlaid sheets provides a great number of fine through-holes, the ion
20 transmission in electrolyte composite 14 isn't blocked. So, the capacitors show a reduced resistance loss, and an improved anti-short circuiting performance.

Now in the following, the present embodiment is described more in detail using practical examples.

25 In the first place, the sample groups 1 - 3 are described. Positive foil 11A of the samples is made of aluminum foil. The foil is roughened by tunnel-shape pits formed vertically from the surface through DC etching process. And then, a dielectric

oxide film (formation voltage 520V) is provided through anode oxidation process. Positive foil 11A thus prepared and negative foil 11C of AC-etched aluminum foil are wound together with intervening separator 11S (50 μ m thick, basis weight 5 25g/m²). The basis weight is the product of density by thickness. Capacitor elements 11 are provided in this way. Materials used for separator 11S are 1) rayon fiber 2) cotton linter 3) double sheets of kraft and hemp 4) double sheets of Manila jute and esparto.

10 Capacitor elements 11 are impregnated with solutions for forming electrolyte composites 14 of sample groups 1 - 3, as shown in Table 1. The variation of acrylic ester derivative in chemical formula (1) is shown in Table 2, variation of acrylic ester derivative in chemical formula (5) in Table 3. 15 The solution for forming electrolyte composites 14 is adjusted so that the water content is 2wt%.

Respective capacitor elements 11 are inserted in bottomed cylindrical metal cases 16 made of aluminum. The open end of metal case 16 is sealed with sealing plate 15 of 20 resin-vulcanized butyl rubber, through curling process. Composition of the sealing member is; butyl rubber polymer 30 weight %, carbon 20 weight % and inorganic filler 50 weight %. The hardness is 70 IRHD[international rubber hardness unit]. Capacitor element 11 may be sealed, instead of using metal case 25 16 and rubber sealing plate 15, with a ceramic, a resin laminate metal foil, etc., in so far as they accomplish the tight sealing.

And then, the sample capacitors are heated at a certain

specific temperature to form electrolyte composite 14 in the inside and the outer surface of capacitor elements 11. Capacitor elements 11 are fixed to the inner surface of metal case 16. The sample capacitors of sample groups 1 - 3 are
5 provided in this way.

Besides the above samples, comparative sample group 1 and comparative sample 2 are prepared for the sake of comparison. Comparative sample group 1 use the same separator as that for sample groups 1 - 3. Comparative sample 2 uses a Manila paper
10 separator (50 μ m thick, basis weight 25g/m²). Also shown in Table 1 are composition of solutions to be impregnated in the capacitor elements of comparative sample group 1 and comparative sample 2. The other items regarding the structure and the method of manufacturing remain the same as those for
15 the sample groups 1 - 3.

Table 1

	Contents of Solution	Composition wt%	Conductivity mS/cm
Sample Group 1	Ethylene glycol	78.8	2.2
	Ammonium benzoate	10	
	Formula(1) No.1 of Table 2	10	
	Formula(5) No.11 of Table 3	1	
	Polymerization initiator	0.2	
Sample Group 2	Ethylene glycol	72.8	2.0
	Ammonium benzoate	10	
	Formula(1) No.3 of Table 2	12	
	Formula(5) No.12 of Table 3	5	
	Polymerization initiator	0.2	
Sample Group 3	Ethylene glycol	59.8	3.2
	Ammonium benzoate	10	
	Formula(2)R1:C ₂ H ₅ n=1	20	
	Formula(6)R3:CH ₃	10	
	Polymerization initiator	0.2	
Comparative Sample Group 1	Ethylene glycol	75	2.3
	Ammonium azelate	10	
	Alkylcellulose	15	
Comparative Sample 2	Ethylene glycol	77.8	2.8
	Ammonium adipate	10	
	Formula(1) No.9 of Table 2	10	
	Formula(5) No.13 of Table 3	2	
	Polymerization initiator	0.2	

5

Table 2

No.	R1	AO 1	
		Species (Added mol no.) Conformation	Molecular Weight
1	CH ₃ -	EO (1.0)	130
2	CH ₃ -	EO (2.0)	174
3	CH ₃ -	EO (4.5)	284
4	H-	EO/PO (3.5/2.5) random	363
5	CH ₃ -	EO (8.0)	438
6	CH ₃ -	EO/TMO (8.4/2.7) random	600
7	CH ₃ (CH ₂) ₂ -	EO/PO (14.8/6.0) block	1100
8	CH ₃ -	EO/PO (85.2/15.5) random	4700
9	CH ₃ -	PO (8.0)	550

Table 3

No.	R3	A02	
		Species (Added mol no.)	Conformation
10	CH ₃ -	EO (2)	Molecular Weight
11	CH ₃ -	EO (4)	242
12	CH ₃ -	EO (9)	330
13	C ₃ H ₇ -	EO/PO (51.1/10.4)	466
14	H-	EO/PO (11.9/16.8)	3000
15	CH ₃ -	EO(13)	1700
16	C ₂ H ₅ -	EO/PO (14.6/6.0)	726
			1000

EO: Ethylene oxide PO: Propylene oxide

TMO: Tetramethylene oxide

Sample electrolytic capacitors are manufactured 20
 5 pieces for each of the categories, sample groups 1 - 3,
 comparative sample group 1 and comparative sample 2. These
 samples are life-tested, and the test results are shown in Table
 4 with respect to the spark voltage of the electrolyte
 composites. Ratings for each of the sample electrolytic
 10 capacitors are 400V, 47 μ F; test temperature at the ripple load
 test is 105°C.

Table 4 indicates that electrical characteristics such
 as tangent of the loss angle ($\tan\delta$) and leak current (LC) of
 electrolytic capacitors in the sample groups 1 - 3 are identical
 15 to those in comparative sample group 1 and comparative sample
 2. However, there is a significant difference regarding the
 long-time stability of electrolytic capacitors in a high
 temperature environment. All of the sample capacitors in
 comparative sample group 1 short-circuit during aging on rated
 20 voltage in the normal room temperature; meanwhile, those in
 comparative sample 2 showed frequent short-circuit troubles
 during life test. On the other hand, those in the sample groups

1 - 3 remain d to be quite stabile, percentage of change in capacitance (ΔC) are small.

Table 4

	Separator	Initial		5000 hr after Ripple Load in 105° C			Sparking Voltage V
		$\tan\delta$ %	LC μ A	ΔC %	$\tan\delta$ %	LC μ A	
Sample Gr up 1	1	4.3	28	-0.9	6.7	13	480
	2	4.1	24	-0.7	6.4	10	
	3	4.1	26	-0.8	6.6	12	
	4	4.2	25	-0.8	6.5	11	
Sample Group 2	1	4.3	23	-0.5	6.6	12	460
	2	4.2	22	-0.8	6.2	10	
	3	4.3	23	-0.8	6.3	11	
	4	4.3	24	-0.7	6.4	11	
Sample Group 3	1	4.1	25	-0.4	6.8	14	500
	2	4.0	22	-0.3	6.3	11	
	3	4.1	24	-0.4	6.6	12	
	4	4.1	23	-0.5	6.5	12	
Compa-rative Sample Group 1	1	All short-circuited during aging					430
	2	All short-circuited during aging					
	3	All short-circuited during aging					
	4	All short-circuited during aging					
Compa-rative Sample 2	Manila paper	3.9	32	Test terminated due to frequent short-circuiting			420

5 From the comparison of sample groups 1 - 3 with comparative sample group 1, it is known that electrolyte composite 14 formed of the matrix of acrylic ester copolymer offers an improved high temperature stability. The comparison of sample groups 1 - 3 with comparative sample 2 tells that
10 it is essential to form electrolyte composite 14 with the matrix of acrylic ester copolymer and to select appropriate materials for the separator. Namely, by using rayon fiber, cotton linter , or by using sheets of cellulose fibers overlaid, for

the separator 11S, the above advantages can be implemented.

Now, samples 4 - 7 are described. Positive foil 11A for the samples is also made of aluminum foil. After the surface roughening through AC etching, dielectric oxide film (formation voltage 90V) is provided through anode oxidation process. Positive foil 11A thus prepared and negative foil 11C of AC-etched aluminum foil are wound together with an intervening separator (50 μ m thick, basis weight 25g/m²) made of rayon fiber and hemp mixed. Capacitor element 11 is manufactured in this way. The electrolytic capacitors are provided in the same way as in sample groups 1 - 3. For the sake of comparison, comparative sample 3 is prepared. The comparative sample 3 uses a hemp paper (50 μ m thick, basis weight 25g/m²). Compositions of the solutions for forming electrolyte composites 14 for samples 4 - 7 and comparative sample 3 are shown in Table 5.

Table 5

	Contents of Solution	Composition wt%	Conductivity mS/cm
Sample 4	Ethylene glycol Ammonium adipate Formula(1) No.3 of Table 2 Formula(5) No.13 of Table 3 Polymerization initiator	79.8 5 10 5 0.2	3.2
Sample 5	γ -butyrolactone 1,2,3,4-tetramethyl- imidazolium phthalate Formula(1) No.4 of Table 2 Formula(5) No.11 of Table 3 Polymerization initiator	84.8 10 2 3 0.2	5.0
Sample 6	γ -butyrolactone Methyldiethyamine hydrogen maleate Formula(1) No.9 of Table 2 Formula(5) No.15 of Table 3 Polymerization initiator	74.8 10 5 10 0.2	4.9
Sample 7	Ethylene glycol Diethylmethyamine adipate Formula(2) R1:CH ₃ , n=4 Formula(6) R3:C ₂ H ₅ Polymerization initiator	74.8 10 5 10 0.2	3.0
Comparative Sample 3	γ -butyrolactone Dimethylethylamine phthalate β -1,3-glucan Alkylcellulose	70 10 10 10	3.0

Sample electrolytic capacitors are manufactured for 20 pieces each. Results of life test and spark voltage of 5 electrolyte composites are shown in Table 6. Ratings for each of the sample capacitors are 63V, 330 μ F; test temperature at the DC load test is 125°C.

Table 6

	Initial		5000 hr after DC Load in 125° C				Sparking Voltage V
	$\tan\delta$ %	LC μA	ΔC %	$\tan\delta$ %	LC μA	Appearance	
Sample 4	3.7	37	-0.3	7.0	12	no problem	250
Sample 5	2.9	35	-0.6	6.3	14	no problem	70
Sample 6	2.8	35	-0.4	6.4	18	no problem	70
Sample 7	3.4	33	-0.7	6.6	11	no problem	180
Compa- rative Sample 3	15.0	45	Wide fluctuation in the characteristics				70

Table 6 tells that the electrical characteristics of electrolytes in samples 4 - 7 are identical to those of comparative sample 3. However, there is a significant difference regarding the long-time stability of electrolytic capacitors in high temperature. Comparative sample 3 showed wide fluctuation in the characteristics during life test, whereas samples 4 - 7 stayed quite stable.

Thus, a sheet of rayon fiber containing at least one kind of cellulose fiber may be used for separator 11S. Cotton linter may be used in place of the rayon fiber for the same advantages.

Next, sample groups 8 - 11 are described. Capacitor elements 11 in these samples remain the same as those in sample groups 1 - 3, with the exception in separator 11S. In sample group 8, cotton linters of different basis weights are used as separator 11S. In sample 9, mixtures of rayon fiber and Manila paper having different basis weights are used. In sample 10, mixtures of cotton linter and kraft paper having different basis weights are used. In sample group 11, various

combinations of rayon fiber, cotton linter, Manila jute, kraft, hemp and esparto are used as separator 11S, as shown in Table 9, each one of the combinations having the same basis weight. For the sake of comparison, comparative sample 4 is prepared.

5 Comparative sample 4 uses a sheet of rayon fiber (basis weight 22.5g/m²) as a separator. Using the above capacitor elements 11, the sample electrolytic capacitors are manufactured in the same way as sample groups 1 - 3. Compositions of the solutions for forming electrolyte composites 14 in sample groups 8 - 11

10 and comparative sample 4 are shown in Table 7.

Table 7

	Contents of Solution	Composition wt%	Conductivity mS/cm
Sample Group 8	Ethylene glycol Ammonium benzoate Formula(2) R1:CH ₃ , n=4 Formula(6) R3:C ₂ H ₅ Polymerization initiator	59.8 10 20 10 0.2	3.2
Sample Group 9	Ethylene glycol Ammonium 1,7-octanedicarboxylate Formula(2) R1:C ₂ H ₅ , n=3 Formula(9) R1:H Polymerization initiator	75.8 10 12 2 0.2	1.8
Sample Group 10	Ethylene glycol Ammonium azelate Formula(1) No.1 of Table 2 Formula(6) Polymerization initiator	83.8 10 5 1 0.2	2.8
Sample Group 11	Ethylene glycol Ammonium 1,7-octanedicarboxylate Formula(1) No.1 of Table 2 Formula(5) No.12 of Table 3 Polymerization initiator	75.8 10 12 2 0.2	2.0
Comparative Sample 4	Ethylene glycol Ammonium azelate Alkylcellulos	75 10 15	2.3

Sample electrolytic capacitors are manufactured for 20 pieces each. Results of the life test are shown in Tables 8 and 9. Ratings for each of the sample electrolytic capacitors are 400V, 330 μ F; test temperature at the DC load test is 125°C.

5 The electrolyte sparking voltages in sample groups 8, 9, 10, 11, and comparative sample 4 are 500V, 500V, 450V, 510V and 430V, respectively.

Table 8

	Separator	Basis Weight g/m ²	Initial		5000 hr after DC Load in 125°C			
			$\tan\delta$ %	LC μ A	ΔC %	$\tan\delta$ %	LC μ A	Appearance
Sample Group 8	Cotton Linter	70.0	21.0	24	-0.8	32.2	9	too much $\tan\delta$
		55.0	10.5	26	-0.6	17.0	10	no problem
		30.0	4.1	29	-0.8	7.1	9	no problem
		4.5	3.6	31	-0.7	5.3	8	no problem
		0.6	2.1	35	-0.8	3.6	7	no problem
		0.01	1.7	38	-0.8	2.1	6	no problem
		0.005	1.4	38	All short-circuited			
Sample Group 9	Mixed sheet of Rayon and Manila	55.0	9.2	25	-0.7	16.6	11	no problem
		30.0	4.0	27	-0.8	6.9	8	no problem
		1.0	2.8	29	-0.7	3.2	7	no problem
		0.01	1.9	32	-0.6	1.9	6	no problem
Sample Group 10	Mixed sheet of Cotton Linter and Kraft	55.0	9.7	27	-0.8	16.9	12	no problem
		30.0	3.8	29	-0.7	7.0	10	no problem
		1.0	2.7	32	-0.6	4.8	9	no problem
		0.01	1.8	33	-0.6	2.0	8	no problem

Table 9

	Separator	Basis Weight g/m ²	Initial		5000 hr after DC Load in 125°C			
			$\tan\delta$ %	LC μ A	ΔC %	$\tan\delta$ %	LC μ A	Appearance
Sample Group 11	Double sheet of Rayon, and mixture of Kraft and Hemp	22.5	4.5	27	-0.6	7.2	9	no problem
	Double sheet of mixture of Rayon and Kraft, and Esparto	22.5	4.4	26	-0.7	15.8	8	no problem
	Double sheet of Rayon, and mixture of Hemp and Esparto	22.5	4.1	25	-0.6	16.3	8	no problem
	Double sheet of mixture of Rayon and Hemp, and Manila	22.5	4.2	24	-0.6	16.3	8	no problem
	Triple sheet of Rayon, and Kraft, and Hemp	22.5	4.	25	-0.6	16.3	8	no problem
	Double sheet of Cotton Linter, and mixture of Kraft and Hemp	22.5	4.2	22	-0.6	15.6	7	no problem
	Double sheet of mixture of Cotton Linter and Kraft, and Esparto	22.5	4.1	25	-0.7	16.0	8	no problem
	Double sheet of Cotton Linter, and mixture of Hemp and Esparto	22.5	4.3	26	-0.5	16.2	8	no problem
	Double sheet of mixture of Cotton Linter and Hemp, and Kraft	22.5	4.2	25	-0.7	15.9	7	no problem
	Double sheet of Manila, and Kraft	22.5	4.3	23	-0.6	15.6	8	no problem
	Triple sheet of Manila, Kraft, and Hemp	22.5	4.1	24	-0.8	15.3	7	no problem
	Double sheet of mixture of Manila and Kraft, and Hemp	22.5	4.2	23	-0.6	15.5	8	no problem
	Double sheet of mixture of Kraft and Hemp, and Esparto	22.5	4.2	25	-0.7	15.4	8	no problem
	Double sheet of Rayon, and mixture of Kraft and Hemp (reinforced)	22.5	4.0	23	-0.5	14.8	6	no problem
	Double sheet of mixture of Manila and Kraft, and Hemp (reinforced)	22.5	4.0	21	-0.4	14.3	6	no problem
	Kraft paper	22.5	4.7	27	Wide fluctuation in the characteristics			
Compa-rative Sample 4	Rayon fiber sheet	22.5	8.0	30	All short-circuited			

As Table 8 indicates, among the electrolytic capacitors in sample group 8 using cotton linter separators of different basis weights, those whose basis weight of separator is more than 55g/m² exhibit too high tanδ after DC load test; those at most 55g/m² do not show any problem in the characteristics of finished product, nor in the appearance. Those less than 0.01g/m² totally cause short-circuiting.

As described in the above, the basis weight of separator 11S should preferably be at least 0.01g/m² at most 55g/m². When such a separator of low basis weight is used, conventional liquid electrolyte or polymer electrolyte readily induces the short-circuiting trouble, and unable to maintain the characteristics in a stable state. When electrolyte composite 14 is employed, the separator is provided with the matrix of polymer in a network arrangement. This maintains the physical distance between the electrodes to ensure an improved withstanding voltage. Therefore, the separators of low basis weight, which has not used to be applicable to medium- and high-voltage capacitors, can now be usable for such capacitors. Since use of such separators substantially lowers the share of a separator among the resistance factors within an electrolytic capacitor, both the ESR and impedance can be significantly reduced.

The mixed sheet of rayon fiber, or cotton linter, and cellulose fiber, exemplified in sample group 9 and sample group 10, do not cause any problem in the characteristics, nor in the appearance.

Referring to Table 9, among those capacitors of sample

group 11 in which different kinds of separators each having the same basis weight are used, only the sample capacitor using the single-sheet kraft paper separator exhibits a wide shift in the characteristics during the test. Sample with other
5 separators do not show any problem, nor in the product appearance.

On the other hand, as comparative sample 4 indicates, those that do not use the acrylic ester polymer electrolyte composite totally cause short-circuiting trouble, despite the
10 use of rayon fiber for separators.

As described above, electrolytic capacitors in accordance with the present exemplary embodiment include the above-described electrolyte composite 14. They are provided with the separator formed of rayon fiber or cotton linter, or
15 double or triple sheets of a cellulose fiber, or a mixture of these. These electrolytic capacitors offer an improved high temperature life characteristic. They can be supplied on a stable basis of production.

Some of those in sample group 11 are provided in the sheet
20 of separator 11S with a reinforcement processing. Practically, separators 11S is reinforced by an agent as such: a polyacrylamide polymer, a polyvinyl alcohol polymer, cationic starch, urea, formalin resin, melamine-formalin resin, epoxidized polyamide polyamine, dialdehyde starch, etc. As
25 the result, separator 11S is strengthened in the tensile strength, which enables to use a separator sheet of lower basis weight. Therefore, the ESR and impedance of a capacitor can be further lowered.

In the present embodiment, positive foil 11A is provided with tunnel pits dug from the surface in the direction of depth. This contributes to raise the capacitance generation rate of positive foil 11A.

5 Electrolytic capacitors in the present invention offer a high withstanding voltage, a high heat resisting property, and a high reliability as well as operational safety in terms of operating life time, anti-vibration capability, etc. They are used in new application in the sectors of anti-higher
10 harmonics circuits and vehicles, among other fields.